PROCESS FOR PRODUCING POLYMERIC FILMS HAVING SHAPE-MEMORIZING PROPERTIES

BBACKGROUND OF THE INVENTION:

This invention relates to the production of transparent films by means of radiation curing. The term "shape-memorizing effect" or simply "shape-memorizing properties" as used used herein means the thermoelastic behavior of a material that is plastic at room temperature to deform permanently under an external force exceeding the elastic limit but which is completely restored to the initial shape upon heating to a shape recovery temperature or above.

Heat-shrinkable films are known as high-molecular weight materials that have similar properties to shape-memorizing resins. However, heat-shrinkable films are not completely restored to the initial shape even if they are heated and, in addition, they do not have a clear shape recovery temperature since they shrink gradually with increasing temperature. Because of their thermal elasticity, shape-memorizing resins are currently used in machine parts, medical devices, articles for daily use and toys. Commercial shape-memorizing resins are described in Japanese Patent Public Disclosure Nos. 53528/1984, 293214/1986, 192440/1987 and 179955/1988.

Resins conventionally known to have the shape-memorizing effect include polynorbornane, a styrene-butadiene copolymer, polyurethane and polyisoprene. The use of these resins has been limited since they can only be given the

initial shape by thermal molding or chemical crosslinking. Further, resins shaped by thermal molding are not suitable for use at elevated temperatures and polyisoprene which is shaped by chemical crosslinking has the disadvantage that the shape-recovery temperature cannot be effectively controlled.

SUMMARY OF THE INVENTION:

The present invention has been accomplished under these circumstances and has as an object providing a method in which a liquid resin composition that is readily polymerized by irradiation to form a shape-memorizing resin is either applied to a shaped part or placed between films to be given a specified shape and is subsequently cured by radiation to produce a cured film having the memory of the specified shape. The present inventors investigated the mechanical properties of films produced by curing with radiation and found the following two types of formulations that provided films having the shape-memorizing effect:

(1) a resin composition comprising:

a) an oligomer that has at least one acryloyl or methacryloyl group in the molecule and that has a glass transition temperature, Tg, of no higher than 50°C after polymerization; and

b) a low-molecular weight compound that has in its molecule one reactive double bond capable of copolymerization with the oligomer a) and that has a glass transition temperature, Tg, of at least 90°C after polymerization; or

b') a mixture of two or more low-molecular weight compounds that have in their molecule one reactive double bond capable of copolymerization with the oligomer compound a) and that have a glass transition temperature, Tg, of at lest 90 °C after polymerization; and

(2) a liquid resin composition comprising:

a) an oligomer compound that has at least one acryloyl or methacryloyl group in the molecule and that has a glass transition temperature, Tg, of no higher than 50 °C after polymerization; and

b) a simple urethane adduct of hydroxyethyl acrylate or hydroxyethyl methacrylate and diisocyanate compound;

said liquid resin optionally containing:

c) a low-molecular weight compound that has in its molecule at least one double bond capable of copolymerization with the oligomer compound a).

DETAILED DESCRIPTION OF THE INVENTION:

When the resin composition (1) or (2) is cured after being applied to a shaped part, a replica of the shaped part is obtained as the cured film. The cured film is removed from the shaped part and it can be deformed to any shape under an external force. The film remains deformed at room temperature but upon heating to the shape-recovery temperature or above, the film is restored to the initial shape.

The resin compositions can be applied to the shape part by any of the methods used to apply conventional solvent-type resins. Instead of being applied to shaped